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DEPARTMENT OF MATERIAL SCIENCES
METALLURGY SECTION

ADA101574

9 TECHNICAL REPORT

to

OFFICE OF NAVAL RESEARCH

Contract No. N00014-81-K-0025

11 9 July 1981

DTIC

REF ID:

JUL 17 1981

6 THE LIMITING IR VOLTAGE WITHIN ELECTROLYTE IN CAVITIES DURING
LOCALIZED CORROSION AND HYDROGEN CHARGING OF METALS

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report	2. GOVT ACCESSION NO. AD-A101574	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Limiting IR Voltage Within Electrolyte in Cavities During Localized Corrosion and Hydrogen Charging of Metals	5. TYPE OF REPORT & PERIOD COVERED Technical Progress Report	
7. AUTHOR(s) H. W. Pickering (Dept. of Materials Science & Engineering, The Pennsylvania State University, University Park, PA 16802)	6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Metallurgy Section, 209 Steidle Building The Pennsylvania State University University Park, PA 16802	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
11. CONTROLLING OFFICE NAME AND ADDRESS Metallurgy Branch Office of Naval Research Arlington, VA 22217	12. REPORT DATE July 9, 1981	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	13. NUMBER OF PAGES 7	
16. DISTRIBUTION STATEMENT (of this Report) Distribution of this document is unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Bubbles in pits, Ohmic drop, Corrosion products in cavities, Pitting mechanism E _{x=L} E _{x=0}		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) In-place gas bubbles within pits, crevices and cracks often cause large differences in electrode potential between the base of the cavity ($E_{x=L}$) and the sample surface ($E_{x=0}$). These potential changes are much greater than predicted by existing theoretical calculations which ignore the possibility of a constricted current path. In this paper, a limiting electrode potential, E_{LIM} , within the cavity is identified. It is the potential at which the net current, with respect to that available for flow in (or out of) the cavity, is zero. (i) In the case of a single current-producing reaction within the cavity, E_{LIM} is the potential at which the net current is zero. (ii) In the case of multiple current-producing reactions within the cavity, E_{LIM} is the potential at which the net current is zero. (iii) In the case of a single current-producing reaction within the cavity, E_{LIM} is the potential at which the net current is zero. (iv) In the case of multiple current-producing reactions within the cavity, E_{LIM} is the potential at which the net current is zero.		

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cavity, E_{LIM} is the equilibrium potential of this reaction. (ii) For more than one reaction of the same sign, E_{LIM} will be the least noble equilibrium potential in the case of anodic polarization, and the most noble for cathodic reactions. (iii) When reactions of opposite sign occur in the cavity E_{LIM} will be the mixed potential of these reactions. \leftarrow

The actual electrode potential at the base of the cavity, $E_{x=L}$, can in principle, only approach E_{LIM} . $E_{x=L}$ is established by the electrolyte resistance R and the current I flowing in or out of the cavity, since I tends to decrease as R increases. The latter occurs as the gas bubbles grow and fill the cross section, and the former occurs since an increasing R , and hence IR , causes the local electrode potential to shift toward the equilibrium or mixed potential, i.e., $E_{x=L} = E_{x=0} + IR$. The increasing resistance R tends to dominate, giving an increasing $|IR|$, but then gives way to I which decreases more sharply as $E_{x=L}$ approaches the Tafel region.

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THE LIMITING IR VOLTAGE WITHIN ELECTROLYTE IN CAVITIES DURING
LOCALIZED CORROSION AND HYDROGEN CHARGING OF METALS

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ABSTRACT

In-place gas bubbles within pits, crevices and cracks often cause large differences in electrode potential between the base of the cavity ($E_{x=L}$) and the sample surface ($E_{x=0}$). These potential changes are much greater than predicted by existing theoretical calculations which ignore the possibility of a constricted current path. In this paper, a limiting electrode potential, E_{LIM} , within the cavity is identified. It is the potential at which the net current, with respect to that available for flow in (or out of) the cavity, is zero. (i) In the case of a single current-producing reaction within the cavity, E_{LIM} is the equilibrium potential of this reaction. (ii) For more than one reaction of the same sign, E_{LIM} will be the least noble equilibrium potential in the case of anodic polarization, and the most noble for cathodic reactions. (iii) When reactions of opposite sign occur in the cavity E_{LIM} will be the mixed potential of these reactions.

The actual electrode potential at the base of the cavity, $E_{x=L}$, can in principle, only approach E_{LIM} . $E_{x=L}$ is established by the electrolyte resistance R and the current I flowing in or out of the cavity, since I tends to decrease as R increases. The latter occurs as the gas bubbles grow and fill the cross section, and the former occurs since an increasing R , and hence IR , causes the local electrode potential to shift toward the equilibrium or mixed potential, i.e., $E_{x=L}=E_{x=0}+IR$. The increasing resistance R tends to dominate, giving an increasing $|IR|$, but then gives way to I which decreases more sharply as $E_{x=L}$ approaches the Tafel region.

A decade ago Pickering and Frankenthal (1) showed that gas bubbles accumulate within growing pits and crevices in iron and stainless steel. They suggested that these in-place bubbles are the cause of large changes in electrode potential within the cavity, changes which placed the base of the cavity in or near the Tafel region even when the outer surface potential was far more noble (>1 volt). In other studies during cathodic polarization, bubbles were observed to grow in place until they impinged on the walls

of the cavity, and to be responsible for large changes in potential (2-4). The effectiveness of a bubble to greatly constrict the current-flow path was attributed to its fluid nature, whereby it could readily take the shape and fill the cavity cross-section. For this reason, the gas bubble is considered to be a more effective constriction than is solid corrosion product. Although bubbles are routinely observed to evolve from pits in Al(5) and other of the active metals (6,7), the tendency for the gas to accumulate and become lodged in the cavity is not so well recognized. In general, this favorable situation for large IR voltages, even in electrolytes of high conductivity, needs to be studied more in order to clarify its role in localized corrosion.

Changes in electrode potential (10^2 to 10^3 mV) have been measured during pitting and crevice growth (1,7-12), although reasons other than electrolyte resistance have been offered by some of these authors. The measurement itself, has been confirmed by other independent observations as follows. The walls of pits (in iron and stainless steel) prior to salt film formation were observed to be crystallographically etched although the outer surface was at >1.0 V (SHE). The etching is consistent with dissolution in the active region and, in particular, the Tafel region of the polarization curve, and also with the measured potential deep within the pits (1,13). In addition, hydrogen was identified as the gas coming out of the pits, in agreement with the measured potential in the pits but contrary to the much more noble potentials (>1 volt noble of the hydrogen equilibrium potential) at the outer surface. Identification of the gas as hydrogen is significant for estimation of the voltage change within the cavity when the electrode potential of the outer surface is noble to the hydrogen evolution equilibrium potential. Then, the voltage change is at least as large as the difference between the external surface potential and the hydrogen equilibrium electrode potential. This same situation has recently been reported for Al (14). These authors observed the evolution of H_2 gas from within pits and concluded that large IR voltages existed within the pit since the electrode potential of the outer surface was maintained at 1.7 volts (SHE) or higher, about 2 volts above the potential for H_2 evolution. In accord with this very noble potential on the external surface, H_2 was not formed on it.

In a similar fashion, large in-place gas bubbles and large changes in electrode potential have been observed within crevices during cathodic evolution of hydrogen on iron, copper, and nickel surfaces (2-4). In accord with current flow into the cavity during cathodic polarization, the electrode potential was observed to become more noble with increasing distance into the cavity, in contrast to a current-flow direction out of the cavity during anodic polarization and a corresponding shift in electrode potential in the less noble direction (15). The magnitude of the measured potential change (0.5 volt) was 5 times larger than the calculated (based on the geometrical cross sectional area) IR voltage (4). For these large shifts in electrode potential,

the bottom of the cavity, in the case of iron and nickel, was in the region of metal dissolution. Accordingly, the bottom of the cavity was etched, and Fe and Ni ions were detected in the electrolyte of the cavity. The shift in electrode potential for Cu, though of the same magnitude, was, on the other hand, not large enough for Cu dissolution. This is consistent with the existence of a limiting potential in the cavity (4,15) which can be approached, but not reached or exceeded, as described in this paper.

From a theoretical point of view, the observation that the current path is constricted by the presence of gas bubbles which occupy the cross section of the cavity means that calculations of IR voltages which are based on the geometrical cross section of the cavity underestimate the actual IR voltage. Many calculations of the potential and concentration variations in pits and crevices are available in the literature (1,11,12,15-18). They all show that for an electrolyte which is a good conductor the ohmic voltage between the growing pit surface and the external metal surfaces is 10 to 10^2 mV. These calculations also assume an unobstructed current path. Thus, in the case of pitting and crevice growth it is well established for samples which are anodically polarized well into the passive region that a discrepancy exists between calculation and experiment -- $<10^2$ mV calculated vs 10^3 mV measured. Even in the case of poorly conducting electrolytes, the ohmic voltage in the cavity (in the absence of constrictions) may be quite small since the ionic concentration and, hence, the conductivity of the electrolyte within a growing pit or crevice increases above that of the bulk solution (1,11,12). The presence of constrictions -- gas bubbles or the less effective solid corrosion products and films -- are therefore necessary to stabilize greatly different cavity and external electrode potentials. Thus, if one takes into account a cross section which may be one, two, or even three orders-of-magnitude smaller over part of the current-flow path, very large IR voltages are calculated during local cell processes. Chang (19) showed this by allowing for the decrease in the cross sectional area of the pit due to the presence of a gas bubble. Ateya and Pickering (4) illustrated the same for hydrogen evolution in a model calculation in which the width of a crack-like slot was allowed to decrease, thereby simulating a growing gas bubble.

As to whether or not it is necessary to maintain the cavity potential in the proximity of the Tafel region in order to maintain a pitting or crevice growth process is less obvious. Without the constriction to provide this electrode potential, one can invoke either or both of the textbook mechanisms for maintaining an active pit or crevice -- the Cl^- ion buildup (along with other anions) in the cavity, or the acidification of the electrolyte within the cavity which occurs except in the case of strong acids -- while the external surface is in the passive region. However, neither of these mechanisms is necessary for pit growth if the potential within the pit is in the moderate overpotential (~Tafel) region.

In view of the fact that IR voltages within cavities can be very large based both on experimental results and model calculations of constricted current flow, the question as to whether or not, in principle, a limiting potential exists in the cavity is important and timely. In considering this question in this paper a physical constrain to the potential shift is identified, and then analyzed in terms of situations encountered during localized corrosion and hydrogen charging of metals. A second question relates to the parameters that are important in establishing the actual electrode potential which exists locally as a function of distance into the cavity.

A Physical Constrain

Let an oxidation or reduction reaction occur at the base of a cavity, $x=L$. The change in electrode potential with distance x into the cavity, $\Delta E(x)$, can be approximately equated to the IR voltage within the electrolyte which fills the cavity, in which case

$$E(x) = E_{x=0} + IR(x) \quad (1)$$

where $E_{x=0}$ is the electrode potential at the opening of the cavity, $E(x)$ is the local electrode potential as a function of distance x into the cavity, I is the current flowing between $x=0$ and $x=L$ with due regard for the current flow direction, and $R(x)$ is the resistance to current flow between $x=0$ and position x . If I or $R(x)$ is large, so is the change in $E(x)$. Conversely, I must be finite or $IR=0$ and $E(x)=E_{x=0}$. Thus, a finite I is the condition which sets the limit on the electrode potential in a cavity, E_{LIM} , a potential which can be approached but not actually reached.

Since the magnitude of $\Delta E(x)$ depends on both I and $R(x)$, the current can be quite small and still produce a large $\Delta E(x)$ if $R(x)$ is large. During development of the gas bubble(s) in the cavity, the increase in $R(x)$ largely controls the increase in $\Delta E(x)$. Eventually, the increasing $R(x)$ shifts the electrode potential existing at the reaction site, $E_{x=L}$, into the Tafel region where the reaction rate I is a strong decreasing function of $E_{x=L}$. In this region I has the greater influence, and counters further increase in the $IR(x)$ voltage. In this way, these two opposing parameters provide for the actual electrode potential $E(x)$ in the cavity which, however, may fluctuate with time under the dynamic conditions which include changing cavity dimensions, distortion of the gas bubble, e.g. by the formation of solid corrosion product, and a changing cavity surface area. The value of $E_{x=L}$ corresponding to the $IR(x)$ voltage will thus always lie between $E_{x=0}$ and E_{LIM} . The latter may be either an equilibrium or a mixed potential depending on the situation, as described below.

The Limiting Potential for Typical Local Cell Processes

Let us consider the case of a single electrochemical reaction in a cavity. This could be metal dissolution which causes growth of a pit, Fig. 1a or hydrogen evolution, Fig. 1b. E_{LIM} for these examples is the equilibrium potential (for the local composition of electrolyte in the cavities) of the respective reaction, metal dissolution (Fig. 1a) or hydrogen evolution (Fig. 1b), since it is at the equilibrium potential that the net current at $E_x=L$ is zero (4,15). Figure 1 describes the situation when $E_{x=0}$ is established by an external power supply or by another (redox) reaction when this reaction occurs at the outer surface, e.g., during some situations of open circuit corrosion.

When two or more reactions of the same sign occur in a cavity e.g., growth of a pit by dissolution of the components of an alloy, E_{LIM} is, in principle, the equilibrium potential of the least noble metal of the alloy. However, the actual $E_{x=L}$ will usually be established by the equilibrium potential of the most noble component, in view of the sharp falloff of the reaction rate with decreasing electrode potential in this potential ("Tafel") region. The same holds for multi cathodic reactions.

The third situation which may exist is the presence in the cavity of two or more electrochemical reactions with at least one reaction producing current of opposite sign to that of the net current. This situation is often encountered in practice during both anodic or cathodic polarization. For example, large IR voltages during the pitting of iron or stainless steel establishes a potential in the pit in the region of hydrogen evolution (1). Similarly, the potential within a crack in iron during Sn electroplating may lie in the region of iron dissolution (2-4,15). These situations are illustrated in Fig. 2, and show that E_{LIM} is not an equilibrium potential, but rather a mixed potential established by the reactions occurring within the cavity, since it is at the mixed potential that the net current at $E_{x=L}$ available for flow in or out of the cavity is zero.

Open circuit pitting corrosion is considered above for the situation that the cathodic reaction occurs entirely on the outer surface, corresponding to the situation in Fig. 1a. However, when some of the cathodic reaction occurs in the pit, the current flowing out of the pit is decreased in proportion to that fraction of the cathodic current which occurs within the pit, and the limiting potential is the mixed potential of the reactions occurring within the cavity. If all of the cathodic reaction occurs within the cavity, there is no net current flowing in or out of the cavity with the result that E_x is the mixed electrode potential of the anodic and cathodic reactions occurring within the cavity at x.

ACKNOWLEDGEMENT

Financial support of the Office of Naval Research under Contract No. N000-14-75-C-0264 is gratefully acknowledged.

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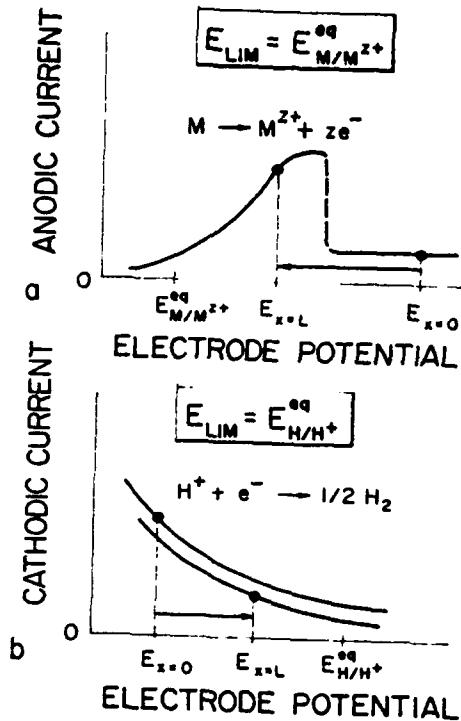


Figure 1.

Schematic illustrating the limiting electrode potential and a typical shift of the electrode potential from the value at the external surface $E_{x=0}$ to that at the bottom of the cavity $E_{x=L}$ (a) during pitting or crevice corrosion, and (b) within a crack during hydrogen evolution. $E_{M/M^{2+}}^{eq}$ and E_{H/H^+}^{eq} are the equilibrium potentials for the composition of the electrolyte in the cavity.

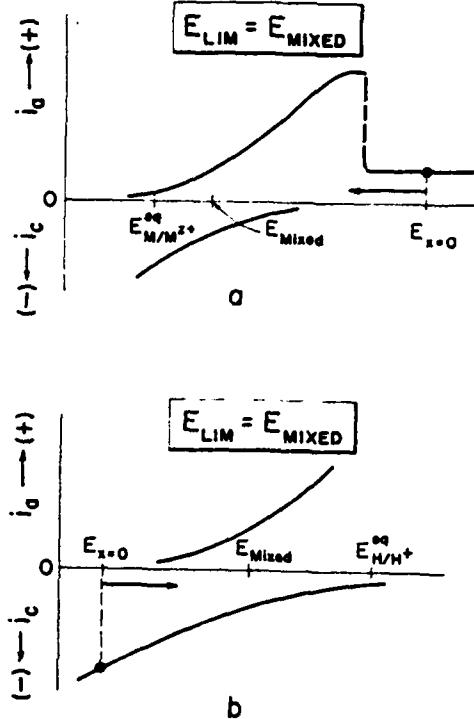


Figure 2.

As in Figure 1 but illustrating that the limiting electrode potential is the mixed potential when reactions of opposite sign occur within the cavity.

